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(71) Applicant: HOWTEK, INC.  
21 Park Avenue  
Hudson New Hampshire 03051(US)

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(72) Inventor: Howard, Robert  
303 East 57th Street  
New York, N.Y. 10022(US)

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(72) Inventor: Hefinski, Richard R.  
56 Gowing Road  
Hudson, NH 03051(US)

(72) Inventor: Menhennett, Herbert E.  
10 Glance Road  
Windham, NH 03087(US)

(74) Representative: Endlich, Fritz, Dipl.-Phys.  
Postfach 1326 Blumenstrasse 8  
D-8034 Germering(DE)

(54) Ink jet color printing.

(57) Color printing characterized by high color density and color contrast is provided by jetting an ink composition composed of an optically clear, phase change base material and a primary subtractive color dye which is soluble in the base material onto the surface of a printing medium to form a multiplicity of closely spaced color dots or spots arranged to define a line or character on the medium. Each dot consists of one or more well defined, optically clear, semitransparent color layers each of which has a different color so that the observed color of each dot is a true subtractive mixture of the colors in the layers. Specific ink compositions are also disclosed.

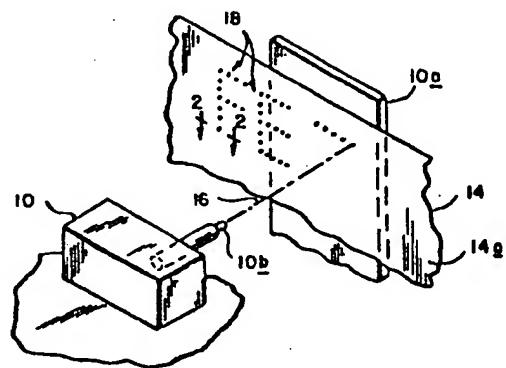


FIG. I

This invention relates to ink jet color printing. It relates more particularly to an ink jet ink composition that produces unusually high quality, high density color printing.

**5 Background of the Invention**

Ink jet printing systems can be divided into the continuous jet type and the drop-on-demand type systems. In the former, a succession of drops are ejected from a small nozzle and projected electrostatically toward a recording medium such as a paper sheet. Selected drops are deflected electrostatically into a gutter, while the remaining drops impinge on and adhere to the sheet to form a character or figure on the paper according to a predetermined dot matrix. In the drop-on-demand or impulse jet type printer, the volume of a pressure chamber filled with ink is suddenly decreased by the impression of an electrical driving pulse and an ink drop is jetted from a nozzle communicating with the chamber. Thus, a single drop of ink is transferred to the paper by a single driving pulse, following which the system returns to its original state. In use, a succession of such droplets is ejected in response to a succession of drive pulses to form a character or figure on the paper according to a predetermined dot matrix. Examples of such printers are disclosed in U.S. Patents 3,653,932; 3,715,219 and in U.S. application Serial No. 571,094, filed January 16, 1984, entitled Droplet Ejector, owned by the assignee of the present application. While the present invention is applicable to both types of ink jet printing, we will describe it specifically in relation to drop-on-demand ink jet printing.

There are several requirements for an ink composition used in an impulse jet printing process. The

physical properties of the ink such as viscosity and surface tension must be within proper ranges if the ink is to be jetted properly. The ink must not clog the nozzle orifice. It must produce images of sufficient optical density. Further, the ink must have a high rate of fixing to the recording medium and not wrinkle, curl or otherwise adversely affect the medium. Further, the ink must be able to form high resolution substantially circular dots on the recording medium which are resistant to water, common solvents, light and abrasion. Since we are concerned here specifically with ink jet color printing, it is desirable if not essential also that the ink be capable of printing in three primary colors as well as in black to produce characters and pictures in a very wide variety of different colors and hues.

Satisfactory color printing by ink jet involves, then, the formation on the recording medium of a multiplicity of colored dots or spots of differing color intensities, depending upon the requirements of the various parts of the character or picture being printed on the medium.

This wide color printing spectrum can be achieved using three or four different color inks either by an additive color mixing process or a subtractive process. In the former, red, green, blue and sometimes black ink drops are deposited on the medium side by side in a dot matrix. The different colored drops are integrated in the observer's eyes so that he perceives a color dependent upon the relative numbers and/or sizes of the different color dots at each part of the printed character or picture. In the subtractive process, the printer deposits ink drops of the primary subtractive colors, namely cyan, magenta and yellow, as well as black, on the medium in superposition in a dot matrix so that each dot is composed of one or more layers, up to

three or four, of printing inks having different color intensities, depending upon the color requirements of the particular part of the character or picture. Each dot layer absorbs a portion of the spectrum of the ambient 5 light illuminating the medium so that the viewer's eye senses the remainder of the light spectrum. Thus, when several ink layers each of a different primary color are present in a single dot in the matrix, several spectral portions are absorbed simultaneously so that a smaller 10 part of the spectrum of the incident light is reflected causing the viewer's eye to sense a mixed color produced by the subtractive mixture of the primary colors.

Thus, true color printing using a subtractive color mixing process depends upon the precision of the printing 15 process as well as the optical properties of the different color printing inks. The color graphics industry prefers to print by subtractive color mixing because the resultant color printing is brighter and more vivid than that resulting from additive color mixing, 20 particularly when the power of the ambient light is relatively low.

Presently, two different types of inks are usually used for ink jet printing, namely water-based inks and oil-base inks and there are many known water- and oil-based inks that can be jet-printed onto a printing medium 25 to produce characters and pictures in color by both the additive and the preferred subtractive color mixing processes. However, such inks have certain drawbacks. More particularly, water-based inks exist on the medium, 30 usually paper, as very thin layers and they get imbibed into the paper. The resultant interaction of the water and the paper fibers distorts the paper. It also results in the incident light being reflected diffusely from the color dots so that the observed printed colors

- are muted. Of course, the paper can be specially treated to avoid this problem. However, that is a limiting factor and adds to the expense of the color printing process. Oil-based inks also tend to penetrate a paper printing medium producing diffuse reflections which mute the observed colors. Further, they have low surface tensions so that, when deposited on the paper, they tend to wick along the paper fibers resulting in overly large and rather irregular printing dots.
- 10 According it would be desirable to be able to provide subtractive color printing by an ink jetting process which is brighter and more vivid than that produced by conventional ink jet color printing systems. This necessarily involves the providing of an ink
- 15 composition which does not adversely affect the printing medium upon which it is placed and whose colors are not muted or otherwise adversely affected by that printing medium. Preferably also the ink composition should be applicable to ordinary untreated paper which is the most
- 20 common and least expensive printing medium.

#### Summary of the Invention

Accordingly, it is an object of the present invention to provide an ink jet ink which will adhere to the surface of a printing medium to produce color printing having a high optical density.

Another object of the invention is to provide an ink composition that can be jetted onto a printing medium such as ordinary untreated paper stock to produce high resolution printed characters and figures in vivid color.

30 A further object of the invention is to provide a color printing system which produces characters on a recording medium comprised of high resolution colored dots having good circularity.

Still another object of the invention is to provide a jet ink for subtractive color printing whose optical characteristics are not adversely affected by the printing medium to which the ink is applied.

5 Yet another object of the invention is to provide an ink of this type which does not adversely affect the paper or other medium to which it is applied.

Another object of the invention is to provide a jet ink of the type just described which is scratch

10 resistant, substantially unaffected by accidental contact with water and other liquids in common use and is able to withstand the temperature and humidity extremes normally encountered by printed documents.

A further object of the invention is to provide  
15 subtractive color printing by jetting individual ink drops from an ink jet printer to a printing medium to form vivid colored lines and characters composed of closely spaced, well defined dots.

Another object of the invention is to provide  
20 jet-printed colored indicia or printing on ordinary paper characterized by high color brightness, optical density and color contrast.

Other objects will, in part, be obvious and will, in part, appear hereinafter.

25 The invention accordingly comprises the several steps and the relation of one or more of such steps with respect to each of the others, and the apparatus embodying the features of construction, combination of elements and arrangement of parts which are adapted to  
30 effect such steps, all as exemplified in the following detailed description, and the scope of the invention will be indicated in the claims.

Briefly in accordance with the present invention, high quality color printing is produced by jetting

phasechange colored inks in liquid form from a jet printer to a printing medium. Upon contact with the medium surface, the inks set and adhere to that surface so as to form colored printing composed of one or more

5 semitransparent or translucent primary subtractive color layers. Preferably the printing is applied as individual ink drops so that the printing is composed of side-by-side, tiny, well defined, layered dots in a dot matrix arrangement. The printing layers in each dot,

10 each of a different primary color, simultaneously absorb different portions of the ambient light spectrum so that the viewer's eye senses a mixed color produced by the subtractive mixture of the primary colors in those layers. For example, printed dots composed of cyan and

15 magenta layers would absorb the red and green components of the white light spectrum so that those dots would be seen as blue. On the other hand, dots composed of cyan and yellow layers which absorb the red and blue portions of the light spectrum, would be seen as green.

20 The ink composition used in the present process is a so called hot melt or thermoplastic ink with a wax base. It should be mentioned at this point that hot melt inks generally are known and have been used to some extent by the printing industry. Indeed U.S. Patents 3,607,808;

25 3,653,932; 3,715,219 and 4,390,369 disclose various thermoplastic inks suitable for jet printing onto a recording medium. However, such inks have only been applied to the medium as single layers to form black printing i.e., text, or to print side-by-side colored

30 dots which together define the colored character by the additive color mixing process described above. As far as applicants are aware, these prior thermoplastic ink compositions have never been used to produce multilayered

semitransparent color printing by the subtractive color mixing process preferred by printers.

It is a well known fact that the printing and graphic industries have long been dissatisfied with the presently available aqueous and oil-based inks. Tremendous effort and large sums of money have been devoted to developing ink compositions for color printing to alleviate the problems discussed above associated with conventional subtractive color printing inks. Despite this long felt need and despite the large sums of money expended to improve these inks, no one until now has thought to print colored characters and lines on a printing medium by jetting phase-change wax-based inks onto the printing medium in distinct strata or layers, with the different layers being semitransparent and giving color to the printing by subtractive color mixing. One can speculate on the reasons why no one has thought to use phase change wax-based inks in this way. One reason might be that one expects a wax-based ink, like a candle, to be too opaque to transmit sufficient light for effective subtractive color mixing. Also it would not readily occur to one that such wax-based inks could be applied in superimposed layers each having a thinness to permit selective absorption by the different layers. Whatever the reasons, the fact is that as far as applicants are aware, they are the first ones to jet phase-change wax-based inks from a jet printer onto a recording medium in superimposed layers, with each layer being of a different primary color and having a thinness such that the color of the printing is a true subtractive mixture of the colors in the different layers.

Utilization of such wax-based inks in this way in a jet printing process yields several advantages. The

waxed-based ink forming the first dot layer does not penetrate into the recording medium even if that medium is ordinary untreated paper stock. Although the ink is jetted to the recording medium as a heated liquid, as soon as it strikes the relatively cool surface of that medium it sets and adheres to the medium surface without imbibing into the medium so that the resulting printing sits right on that surface. Accordingly, the ink does not distort the medium. Nor does the medium interact with the ink to cause material light scattering which could mute the color of the printing. Still further, since each ink layer sets immediately upon reaching the medium surface or a previously applied layer, each layer is well defined and there is no turbid mixing of the ink colors. Rather there is a definite boundary between the adjacent differently colored ink layers so that the perceived color of the printing is a true subtractive mixture of the colors of those layers. Therefore, printing can be applied to almost any printing medium, including coarse untreated paper stock, which is well defined, unusually bright and vivid and has high color contrast. Also, of course, since the ink compositions are waxed-based, the resulting print or indicia on the printing medium is scratch resistant and is substantially unaffected by common fluids, including water, and by the temperatures that would normally be encountered by printed matter in the mails and elsewhere.

Brief Description of the Drawing

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description, taken in connection with the accompanying drawing, in which:

FIG. 1 is a diagrammatic view of a color printing system embodying the principles of this invention, and

FIG. 2 is a sectional view on a much larger scale taken long line 2-2 of FIG. 1.

5 Detailed Description of the Preferred Embodiment

Refer now to FIG. 1 of the drawing which shows a system for color printing in accordance with our technique. It comprises a printer 10 which applies color printing 12 to a recording medium 14 such as sheet of ordinary paper positioned against the printer platen 10a. The printer 10 specifically illustrated is an impulse jet or a drop-on-demand type printer. It may be a conventional jet printer or be a printer similar to the one disclosed in the aforesaid pending application.

15 Suffice to say that printer 10 contains separate supplies of differently colored thermoplastic phase change inks to be described in more detail later. The inks are maintained at an elevated temperature so that they can be jetted as individual drops 16 from separate printer nozzles 10b to the surface 14a of recording medium 14 in response to controlled drive signals applied to the printer. The ink drops impinge on and adhere to the medium surface 14a to form a multiplicity of dots or spots 18 spaced closed together in a dot matrix

20 arrangement so that together the dots form one or more colored lines, characters or fields as determined by the signals controlling the printer.

25

Each of the differently colored inks jetted onto medium 14 is a non-aqueous thermoplastic or hot melt ink composed of a wax base material or carrier and a dye. The base material exists in a liquid phase when heated in printer 10 to a relatively high temperature (e.g. above 150° F) and changes immediately (i.e. in less than

100 ms) to a solid phase upon striking the cooler surface of medium 14. At the jetting temperatures, the base material should have a viscosity of 1 to 50 centipoise and a surface tension of 20 to 50 dynes/cm<sup>2</sup> such that the 5 ink can be propelled electrostatically by the printer 10 as small drops 16 to the recording medium to form dots or spots 18 on the medium surface 14a which are of a uniform small size (e.g., .5 to 8 mils). Also, when the base material sets it is relatively hard and scratch 10 resistant. Thus the present ink, and particularly its base material, should have all of the desirable properties of the thermoplastic inks described in the above-mentioned patents used in uni-color or additive color printing. In addition, however, the base material 15 of the present ink composition must be optically clear or non-turbid in both its solid and liquid states so that it is quite transparent to light energy and produces minimal light scattering. A suitable optically clear, phase change base material for our purposes is a fatty acid 20 such as stearic acid.

The dye compound of each ink composition must be soluble in the base material in both phases of that material and not change the viscosity of the base material appreciably. Sufficient dye should be dissolved 25 in the base material so that the jetted colored ink dots or spots 18 are intense and vivid with reflection densities (ANSI) of 1 to 3 and preferably in excess of 2. Since we are concerned here with printing by subtractive color mixing, the dye colors are usually the primary 30 colors consisting of cyan, magenta, yellow and also black. As with any other dye used in color printing, the dye in the wax-based ink compositions here should have good post print stability. That is, it should be able to withstand the temperatures normally encountered by

printed materials in the mails and during handling, which  
are usually no higher than 85° F.

The following are examples of suitable dyes:

5

	<u>Cyan</u>	<u>Magenta</u>	<u>Yellow</u>	<u>Black</u>
	Atlasol	Atlasol	Atlasol	Atlasol
	Spirit blue THF	Spirit Magenta M	Spirit yellow BB	Black M
10				
	Waxoline	Rhodanine B	Saviny1	Saviny1
	Blue AP.FK.		Yellow RLSN	Black RLS
	Alphazurine		Zapon	
15	Blue FGND		Yellow 073	

Refer now to FIG. 2 which shows in greater detail the plural layer structure of the dots 18. Each dot jetted onto the medium surface 14a comprises one or more 20 precisely defined ink layers, with each layer being of a different primary color. Thus the dot specifically illustrated in FIG. 2 has three such layers 18a, 18b and 18c colored cyan, magenta and yellow respectively. The color density of each layer and its transparency are 25 determined primarily by the thickness of that layer and that thickness can be varied by controlling the temperature (to vary viscosity) and size of the ink drop 16 that forms that layer. The thicknesses of the layers are quite small, i.e. less than 5 mil in order to obtain 30 the requisite translucency. However, each layer should contain sufficient dye to have the required color density as noted above. Also, it should be noted that the thicknesses of the layers in a given printed dot 18 may be different depending upon the color requirements and,

in fact, that is usually the case. For example, in a print specimen made in accordance with this invention, the ink dots comprising the printing may be composed of a cyan layer closest to the surface 14a having a thickness 5 of 2 mil, an intermediate yellow layer superimposed on the cyan layer having a thickness of 1 mil and an outer magenta layer 18c superimposed on the layer 18b and having a thickness of 0.3 mil, with the dots as a whole) being perceived as having a greenish color.

10 The successively jetted ink drops 16 comprising each printed dot 18 on medium 14 are spaced in time so that each drop sets before the next drop arrives so that the first ink layer 18a sits right on the surface 14a of the printing medium and so that all the layers form well-defined superimposed strata with definite boundaries 22a, 22b and 22c as clearly seen in FIG. 2. Thus, the ink in the first layer 18a is not imbibed into the printing medium 14 nor does it tend to wick along the fibers of that medium which phenomena could give rise to light scattering in the layer 18a. Further, since there is no interaction between the first ink layer 18a and the printing medium, almost any material can be used for that medium, even coarse paper stock, or open-weave fabric without appreciable loss of color brightness. This 25 laying down of the different color inks as defined strata with sharply defined planar boundaries also insures that there is no turbid mixing of the ink colors between adjacent layers. Resultantly, each semitransparent ink layer 18a, 18b and 18c transmits light specularly rather than diffusely so that it functions as a high quality optical filter that filters out a well-defined portion or component of the white light spectrum. As a consequence, the layers comprising each dot 18 achieve true subtractive color mixing of the colors in those layers to

produce a wide variety of selected dot colors which are especially bright and vivid. Accordingly, when different ink color combinations are used for the ink layers in adjacent printed dots 18, there is excellent color

5 contrast between these different color dots.

Utilizing our printing process, then, high quality printed documents can be produced in color whose printed colored lines and color fields are characterized by high optical density and color brightness even when the

10 ambient light intensity is relatively low. Accordingly, our process should find wide acceptance in the color printing and graphics industry which has long sought to provide high quality color printing by a subtractive color mixing process without incurring the difficulties  
15 stemming from the use of aqueous and oil-based printing inks.

Further, although we have specifically described ink compositions utilizing a wax as the ink base material or dye carrier, it is also possible to substitute other  
20 natural and synthetic, optically clear phase change materials such as oleic acid, polyethylene and blends or mixtures of such materials.

It will thus be seen that the objects set forth above, among those made apparent from the preceding  
25 description, are efficiently attained, and, since certain changes may be made in the above method and in the above construction without departing from the scope of the invention, it is intended that all matter contained in the above description or shown in the accompanying  
30 drawing be interpreted as illustrative and not in a limiting sense.

It is also to be understood that the following claims are intended to cover all of the generic and specific features of the invention herein described.

X6 -1-

1 1. A method of color printing on a printing medium  
2 comprising the steps of

- 3       A. applying a first color phase-change ink as a  
4       liquid onto an area of said medium so that the  
5       first ink forms a first, thin, solid,  
6       semi-transparent, well-defined, optically clear  
7       ink layer that adheringly covers without  
8       appreciably penetrating or distorting said  
9       medium area; and
- 10      B. applying a second color phase-change ink as a  
11     liquid onto the exposed surface of said first  
12     ink layer in superposition therewith so that the  
13     second ink forms a second, thin, solid, semi-  
14     transparent, well-defined, optically clear ink  
15     layer that adheringly covers said first ink  
16     layer whereby the ink layers transmit ambient  
17     light substantially specularly and produce  
18     subtractive color printing on said medium area  
19     characterized by high color density and  
20     brightness.

1 2. The method defined in claim 1 and including the  
2 additional step of superimposing one or more additional  
3 said ink layers of different colors to said second ink  
4 layer.

1 3. The method defined in claim 1 wherein said ink is  
2 applied to said medium by jetting the inks onto the  
3 medium area as successive liquid drops each of which  
4 solidifies prior to the impingement of a succeeding drop  
5 at that area of the medium.

1 4. The method defined in claim 3 comprising the  
2 additional step of jetting the inks so that said  
3 successive liquid drops have different sizes whereby  
4 selected ink layers have different thicknesses.

1 5. An ink composition for ink jet color printing  
2 comprising

- 3 A. a phase change base material which can exist in  
4 solid and liquid phases and which is optically  
5 clear in both phases; and
- 6 B. a primary subtractive color dye which is soluble  
7 in the base material in both material phases and  
8 does not appreciably affect the viscosity of the  
9 base material, said ink composition having a  
10 viscosity when the base material is in the  
11 liquid phase of from one to fifty centipoise and  
12 an optical density of from one to three.

1 6. The ink composition defined in claim 5 wherein the  
2 base material is a fatty acid.

1 7. The ink composition defined in claim 6 wherein the  
2 base material is stearic acid.

1 8. The ink composition defined in claim 5 wherein the  
2 base material comprises a thermoplastic.

1 9. The ink composition defined in claim 8 wherein the  
2 base material comprises polyethylene.

1 10. The ink composition defined in claim 5 wherein the  
2 base material comprises a blend of natural and/or  
3 synthetic phase change materials.

1 11. Color printed material comprising  
2 A. a printing medium;  
3 B. a first thin layer of a phase change primary  
4 subtractive color printing ink of a first color  
5 adhered to a surface area of the medium, said  
6 first layer having a well defined boundary  
7 substantially at the medium surface;  
8 C. one or more additional thin layers of a phase  
9 change printing ink, each additional layer  
10 having a different primary subtractive color  
11 different from said first color superimposed on  
12 the first ink layer, each said additional layer  
13 having a well defined boundary with any adjacent  
14 layer and each of said layers being optically  
15 clear and non-turbid so that specular reflection  
16 of ambient light occurs in each layer whereby  
17 the observed color of the print on said surface  
18 area is a vivid subtractive mixture of the  
19 colors of all of said ink layers.

1 12. The material defined in claim 11 wherein each phase  
2 change ink comprises

- 3 A. a thermoplastic base material which can exist in  
4 solid and liquid phases and which is optically  
5 clear in both phases; and
- 6 B. a primary subtractive color dye which is soluble  
7 in the base material in both material phases and  
8 does not appreciably affect the viscosity of the  
9 base material, said ink composition having a  
10 viscosity when the base material is in the  
11 liquid phase of from one to fifty centipoise and  
12 an optical density of from one to three.

1 13. The material defined in claim 11 wherein selected  
2 ones of said ink layers have different thicknesses.

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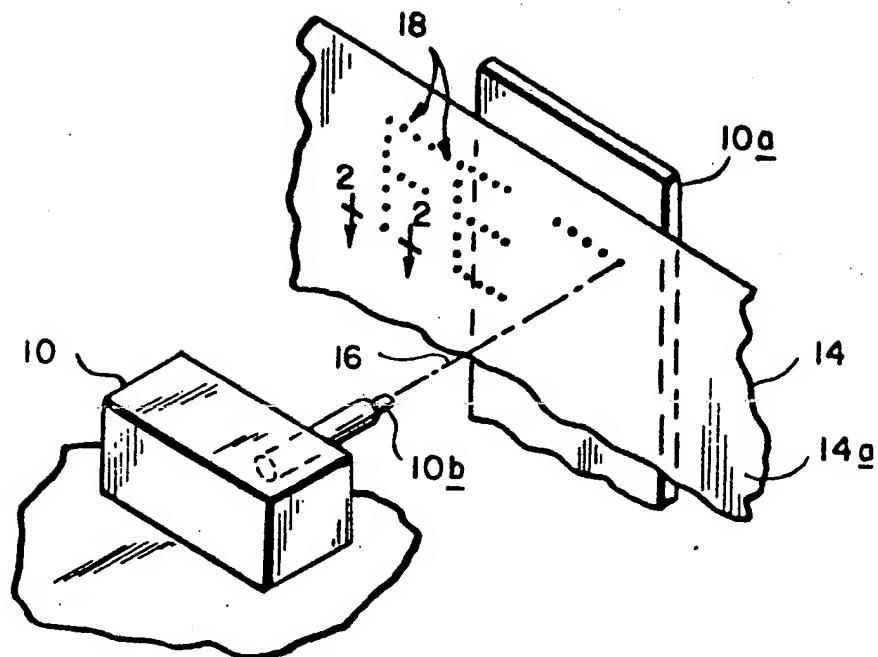


FIG.1

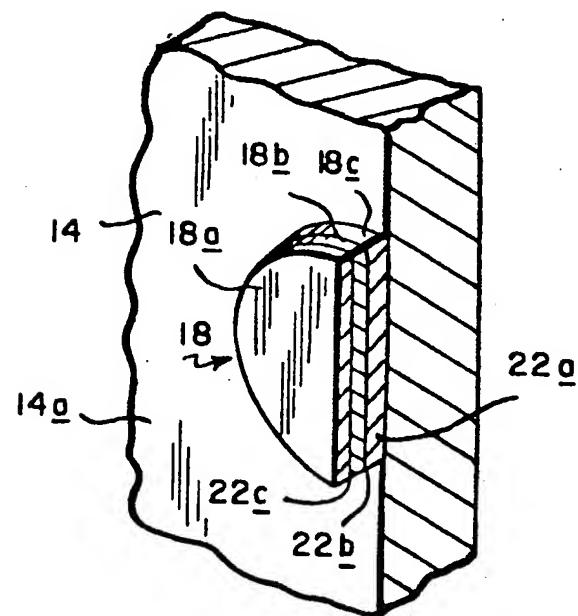


FIG.2

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(71) Applicant: HOWTEK, INC.  
21 Park Avenue  
Hudson New Hampshire 03051(US)

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(72) Inventor: Howard, Robert  
303 East 57th Street  
New York, N.Y. 10022(US)

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(72) Inventor: Hellinski, Richard R.  
56 Gowing Road  
Hudson, NH 03051(US)

(84) Designated Contracting States:  
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(72) Inventor: Menhennett, Herbert E.  
10 Glance Road  
Windham, NH 03087(US)

(54) Ink jet color printing.

(74) Representative: Endlich, Fritz, Dipl.-Phys.  
Postfach 1326 Blumenstrasse 8  
D-8034 Germering(DE)

(57) Color printing characterized by high color density and color contrast is provided by jetting an ink composition composed of an optically clear, phase change base material and a primary subtractive color dye which is soluble in the base material onto the surface of a printing medium to form a multiplicity of closely spaced color dots or spots arranged to define a line or character on the medium. Each dot consists of one or more well defined, optically clear, semitransparent color layers each of which has a different color so that the observed color of each dot is a true subtractive mixture of the colors in the layers. Specific ink compositions are also disclosed.

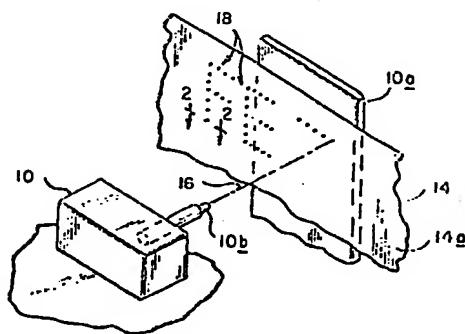


FIG. I

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European Patent  
Office

## EUROPEAN SEARCH REPORT

Application Number

EP 85 11 6340

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
X, Y	GB-A- 543 393 (J.M. HUBER) * Whole document * ---	1-11	C 09 D 11/00 B 41 M 1/18 B 41 J 3/04
X, Y	US-A-2 322 445 (W. HUBER) * Claims; page 2, column 2, lines 58-62 * ---	1-11	
X	PATENT ABSTRACTS OF JAPAN, vol. 7, no. 257 (M-256) [1402], 16th November 1983; & JP-A-58 140 257 (YOKOGAWA DENKI SEISAKUSHO K.K.) 19-08-1983 * Whole document * ---	1-11	
D, X	US-A-3 607 808 (S.P. THOMPSON) * Claims * ---	1,8,9	
X	EP-A-0 099 682 (EXXON) * Claim 1 * ---	1,6,7	
Y	EP-A-0 021 389 (SIEMENS) * Page 2, lines 6-20; claims * ---	1-11	
Y	PATENT ABSTRACTS OF JAPAN, vol. 4, no. 89 (C-16) [571], 25th June 1980, page 135 C 16; & JP-A-55 54 368 (CANON K.K.) 21-04-1980 * Whole abstract * ---	1-11	
A	THE INSTITUTE FOR GRAPHIC COMMUNICATION, CONFERENCE DATA FOR CONTINUING EDUCATION PROGRAM, 1981, pages 1-10; C.A. MUENCH et al.: "Tricolor ink jet systems" * Whole document * ---	1-11	
A	TEK 4695, 1983, Tektronix, Inc.; Color graphics copier ---	1-11	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	21-12-1987	RASSCHAERT A.	
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone	T : theory or principle underlying the invention		
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A : technological background	D : document cited in the application		
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P : intermediate document	& : member of the same patent family, corresponding document		



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DOCUMENTS CONSIDERED TO BE RELEVANT			CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	
A	ADVANCED COLOR TECHNOLOGY, specification summary; "Plug in the ACT-1 color copier" ---	1-11	
A	BRITISH STANDARD FOUR-COLOUR AND THREE-COLOUR, LETTERPRESS PROCESS INKS, B.S. 1480 : 1949, pages 2-9, British Standards House, London, GB * Appendix 3 * -----	1-11	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
<p>The present search report has been drawn up for all claims</p>			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	21-12-1987	RASSCHAERT A.	
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